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HAIR-DRESSING RESIN COMPOSITION AND AEROSOL FOAM-TYPE SOAP-FREE
COMPOSITION THEREOF

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HAIR-DRESSING RESIN COMPOSITION AND AEROSOL FOAM-TYPE SOAP-FREE
COMPOSITION THEREOF

[SeihatuyoJushisoseibutu oyobi Soreo Mochiita Aerosol Foam-kata Soap-Free Soseibutu]

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[Amendments have been incorporated into the text of the translation.]

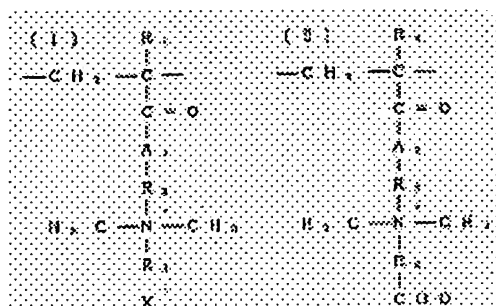
Claims

/11*

1. A hair-dressing resin composition characterized by comprising a 1:2 - 1:10 by weight mixture of cationic/amphoteric polymer consisting 5-60 mol% of cationized repeating unit represented by the following general formula [I] and 95-40 mol% of amphoterized repeating unit

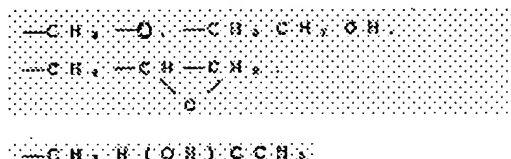
* [Numbers in the right margin indicate pagination of the original foreign text.]

represented by the following general formula [II] and water-soluble anionic polymer and at the same time, being water soluble.

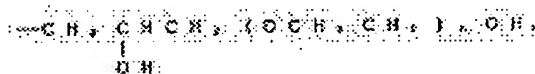


[In the formulas, R_1 and R_4 are H or CH_3 ; R_2 , R_5 and R_6 are alkylene groups of $CH_2-C_4H_6$; R_3 is H, alkyl group of $CH_3-C_4H_8$,

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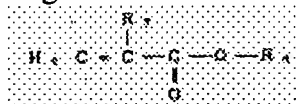
or



(where n is an integer of 1-9); A_1 and A_2 are O or NH; X is Br, Cl, I, CH_3SO_4 , $C_2H_5SO_4$, CH_3COO or $ClCH_2COO$].

2. The hair-dressing resin composition of Claim 1, wherein the water-soluble anionic polymer is a polymer prepared by carrying out solution polymerization of a monomer mixture of the following composition;

(a) monomer represented by the general formula



5-40 wt%

(where R_7 is H or CH_3 , and R_8 is an alkyl group of C_8H_{17} - $C_{18}H_{37}$)

(b) at least one kind of monomer selected from a group comprising acrylic acid, methacrylic acid and itaconic acid: 6-35 wt%

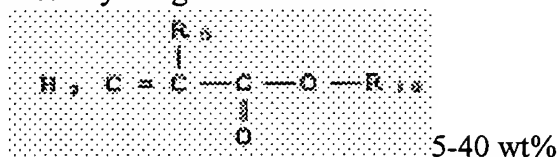
(c) other vinyl monomer: 25-89 wt%

in a water-soluble solvent and adding a water-soluble organic base.

3. The hair-dressing resin composition of Claim 1, wherein the water-soluble anionic polymer is a polymer prepared by carrying out solution polymerization of a monomer mixture of the following composition;

(d) diacetoneacrylamide: 5-88 wt%

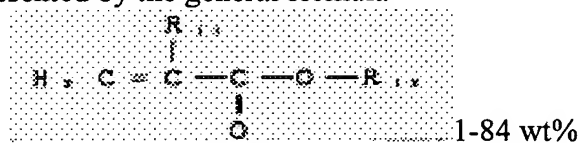
(e) monomer represented by the general formula



(where R₉ is H or CH₃, and R₁₀ is an alkyl group of C₈H₁₇-C₁₈H₃₇)

(f) at least one kind of monomer selected from a group comprising acrylic acid, methacrylic acid and itaconic acid: 6-35wt%

(g) monomer represented by the general formula



(where R₁₁ is H or CH₃, and R₁₂ is an alkyl group of CH₃-C₃H₇)

in a water-soluble solvent and adding a water-soluble organic base.

4. An aerosol foam soap-free composition containing the hair-dressing resin composition of Claim 1, 2 or 3. /2

Detailed explanation of the invention

Industrial application field

This invention pertains to a hair-dressing composition and aerosol foam-type soap-free composition thereof.

Prior art

Various nonionic, anionic, cationic, amphoteric resins and their mixtures have been used previously as a hair-dressing resin.

As a nonionic resin, poly(vinyl pyrrolidone) and poly(vinyl methyl ether) have been known. The former has problems such as its film being hard before moisture absorption, suddenly becoming soft after moisture absorption causing a blocking phenomenon, etc., and the latter has a shortcoming of the effects of moisture absorption larger than those of the former.

As an anionic resin, copolymeric resins having ionic groups such as (meth)acrylic acid, etc., have been known, and there are those liable to be affected by moisture and those not liable to be affected by moisture. Their affinity with hair is weak, and there are shortcomings such as

being liable to cause a flaking phenomenon, lacking smoothness, etc., because it is necessary to form a hard film to improve hair-dressing effects.

As a cationic resin, cationized cellulose, cationized product of vinyl pyrrolidone/dimethylaminoethyl methacrylate copolymer, poly(dimethylallyl ammonium chloride), etc., have been known. These compounds show better affinity to hair than those two kinds described above, and they are also antistatic, but they are liable to be affected by humidity, and there are other shortcomings such as crystallization and solidification with shampoo (anionic) at the time of hair washing, etc.

As an amphoteric resin, monochloroacetic acid-amphoterized products of octylacrylamide/butylaminoethyl methacrylate/(meth)acrylic acid/(meth)acrylate copolymer and dialkylaminoethyl methacrylate/butyl methacrylate/other nonionic monomer copolymer, etc., have been known. These resins show good affinity with hair, the problems of adhesion of foreign objects, dusts, etc., and entanglement of hair strands, etc., are less than those observed in nonionic or anionic resins, and the hygroscopicity is smaller than that of nonionic or cationic resins, but the setting force under high humidity is insufficient. /3

In the case of a mixture of those resins described above, the shortcomings of respective resins can be compensated to some extents, but on the other hand, there is a problem of setting back the advantages of respective resins. A mixture of anionic and cationic resins frequently becomes insoluble due to conflicting ionic characteristics, the setting power is reduced at a high temperature because of high hygroscopicity of the cationic resin, and there are other shortcomings such as reduced affinity with hair, etc. Moreover, there is no problem with respect to compatibility in the case of a mixture of anionic and amphoteric resins, but the advantages of the respective resins are set back, and at the same time, the shortcomings of the resins are not satisfactorily compensated.

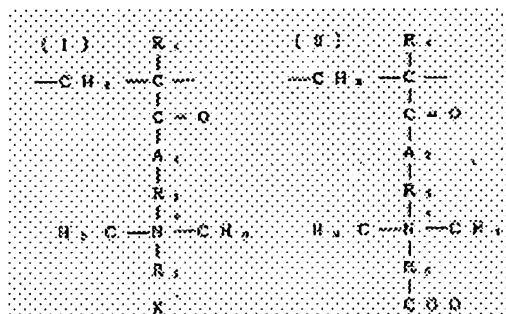
In the case of an aerosol foam composition, the foam is prepared by compounding the hair-dressing resins described above with various surfactants and(or) foaming agents such as nonionic cellulose, etc., and as a result, performance of the hair-dressing resins is reduced. In this case, especially under high humidity, the setting power is reduced due to moisture absorption by the foaming agent such as surfactants, etc., compounded, and there are other problems such as increased viscosity, etc.

Objective of the invention

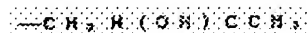
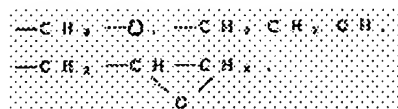
The object of this invention is to provide a hair-dressing resin composition not causing any stickiness or flaking, showing excellent smoothness, exhibiting excellent setting power at a high temperature under high humidity and, at the same time, retaining a good feel and aerosol foam soap-free composition to use it.

Technical means to accomplish the objective and action

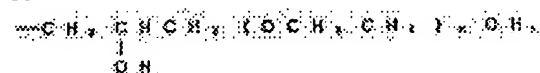
The hair-dressing resin composition of this invention is characterized by comprising a 1:2 – 1:10 by weight mixture of cationic/amphoteric polymer consisting 5-60 mol% of cationized repeating unit represented by the following general formula [I] and 95-40 mol% of amphoterized repeating unit represented by the following general formula [II] and water-soluble anionic polymer and, at the same time, being water soluble.



[In the formulas, R₁ and R₄ are H or CH₃; R₂, R₅ and R₆ are alkylene groups of CH₂-C₄H₆; R₃ is H, alkyl group of CH₃-C₄H₈,



OR



(where n is an integer of 1-9); A₁ and A₂ are O or NH; X is Br, Cl, I, CH₃SO₄, C₂H₅SO₄, CH₃COO or ClCH₂COO].

The cationic/amphoteric polymer described above can be prepared by using a method carrying out cationization and amphoterization after polymerization of monomers corresponding to respective repeating units; cationization and amphoterization of monomers and subsequent polymerization; amphoterization after copolymerization of cationized and unmodified monomers or cationization after copolymerization of amphoterized and unmodified monomers.

As a monomer before modification (cationization or amphoterization) corresponding to the repeating unit represented by the general formula [I] or [II], there are dimethylaminoethyl (meth)acrylate, dimethylaminopropyl (meth)acrylate, dimethylaminoethyl (meth)acrylamide, etc., which may be used alone or concomitantly.

If the content of the repeating unit of the general formula [I] is less than 5 mol% in this invention, the bonding between the cationic/amphoteric and water-soluble anionic polymers becomes weak, the poor smoothness, which is a shortcoming of the water-soluble anionic polymer, is not improved, the flaking phenomenon is not sufficiently reduced, and it is difficult to prepare an aerosol foam soap-free composition. Furthermore, if the content of the repeating unit is over 60 mol%, the mixing stability between the cationic/amphoteric and water-soluble anionic polymers becomes poor, and the water-solubility of the resin composition prepared from these polymers also becomes poor causing a problem in the hair-dressing performance.

As a cationizing agent, there are, for example, acids such as hydrochloric acid, hydrobromic acid, acetic acid, chloroacetic acid, etc. As a quaternary cationizing agent, there are, for example, methyl chloride, methyl bromide, methyl iodide, ethyl chloride, ethyl bromide, propyl chloride, propyl bromide, ethylene chlorohydrin, ethylene bromohydrin, epichlorohydrin, epibromohydrin, propylene chlorohydrin, propylene bromohydrin, benzyl chloride, benzyl bromide, polyethylene glycol monoepoxide, dimethylsulfuric acid, diethylsulfuric acid, etc.

As an amphoterizing agent, there are, for example, neutralized products such as sodium monochloroacetate, potassium monochloroacetate, lithium monochloropropionate, sodium monochloropropionate, potassium monochloropropionate, monochloroacetic acid and ammonia, 2-amino-2-methyl-1-propanol, monoethanolamine, diethanolamine, triethanolamine, 2-amino-2-ethyl-1,3-propanediol, 2-amino-2-ethyl-1-propanol, morpholine, etc.

The cationizing and amphoterizing agents described above are used in a stoichiometric amount or equimolar amount.

Those monomers corresponding to the repeating units represented by the formulas [I] and [II] may be copolymerized in a hydrophilic solvent. As a suitably usable hydrophilic solvent, there are, for example, water, one or more kinds of water-soluble aliphatic alcohols having 1-4 carbon atoms and their mixtures. Incidentally, it may become necessary to select a solvent composition depending on the solubility of monomers after modification. The copolymerization is carried out by using conventional solution polymerization procedures, for example, by dissolving monomers in the solvent described above, adding a polymerization initiator and carrying out heating and stirring under a flow of nitrogen gas after selecting suitable polymerization conditions. As a polymerization initiator, there are, for example, peroxides such as benzoyl peroxide, etc., and azo compounds such as azobisisobutyronitrile, etc.

The copolymerization of monomers is carried out in a state of adding the whole amounts of monomers from the beginning of the polymerization reaction or by dividing monomers according to the kind and (or) amount. The hydrophilic solvent is used in the amount so that the concentration of the polymer formed in the solution is in the range of 30-70 wt%. The mean molecular weight of the polymer is preferably in the range of 10 thousand to 500 thousand.

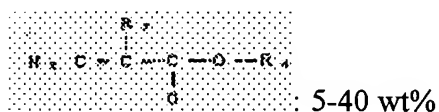
The cationization reaction to use an acid is carried out by adding a solution of the acid in drops to the monomer or polymer while stirring in a solution of hydrophilic solvent under a flow of nitrogen gas and heating the mixture at 60-90°C for 0.5-2 h. The reaction to use a quaternary cationizing agent is carried out by adding a quaternary agent in its vapor form or its hydrophilic solvent solution in drops to a hydrophilic solvent solution of the monomer or polymer while stirring under a flow of nitrogen gas and heating at 70-95°C for 2-10 h.

The amphoterizing reaction is carried out by using an amphoterizing agent having a relatively high boiling point. Similarly to the above reaction with a quaternary cationizing agent, an aqueous or hydrophilic solvent solution or suspension of an amphoterizing agent is added dropwise to a hydrophilic solvent solution of the monomer or polymer while stirring under a flow of nitrogen gas and heating at 70-95°C for 2-10 h. Incidentally, if the amphoterizing agent used is a salt of alkaline metal such as sodium, potassium, lithium, etc., an inorganic salt is precipitated in an aliphatic alcohol as the amphoterization reaction proceeds, thus, it is removed by carrying out centrifugation, filtration or other solid-liquid separation procedures. On the other hand, if the amphoterizing agent is an amine salt or ammonium salt, no organic salt is precipitated as the amphoterization reaction proceeds, and the homogeneous solution formed is usable as it is.

The polymer prepared as described above may be used as it is in a hydrophilic solvent or by removing the solvent and substituting it with water. This cationic/amphoteric polymer is mixed with a water-soluble anionic polymer in a ratio of 1:2 – 1:10 by weight to obtain a hair-dressing composition. If the amount of the cationic/amphoteric polymer compounded is over the ratio of 1:2 by weight, the anionic polymer and resin composition containing it form a sticky film, and the setting power under high humidity at the time of application to hair is reduced. On the other hand, if the amount compounded is below the ratio 1:10 by weight, the film formed becomes hard, the smoothness and handling at the time of application to hair become poor, and it becomes liable to cause flaking.

As a water-soluble anionic polymer, it is possible to use a polymer prepared by carrying out solution polymerization of a monomer mixture of the following composition;

(a) monomer represented by the general formula



(where R₇ is H or CH₃, and R₈ is an alkyl group of C₈H₁₇-C₁₈H₃₇)

(b) at least one kind of monomer selected from a group comprising acrylic acid, methacrylic acid and itaconic acid: 6-35 wt%

(c) other vinyl monomer: 25-89 wt%

in a water-soluble solvent and adding a water-soluble organic base.

If the amount of the monomer (a) compounded is below 5 wt%, the mutual compatibility of the anionic polymer prepared with halogenated hydrocarbon, liquefied petroleum gas, etc., becomes insufficient, the film prepared from the anionic polymer and resin mixture containing it has insufficient softness, and it becomes liable to cause flaking. On the other hand, if the amount compounded is over 40 wt%, the anionic polymer prepared becomes difficult to dissolve in water, and the stickiness of the prepared film is increased. As a monomer (a), there are, for example, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate, cetyl (meth)acrylate, stearyl (meth)acrylate, etc., used alone or concomitantly.

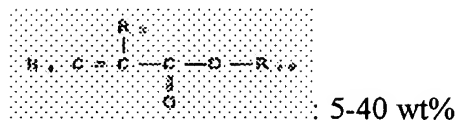
Furthermore, if the amount of the monomer (b) compounded is below 6 wt%, the anionic polymer formed becomes difficult to dissolve in water. On the other hand, if it is over 35 wt%, the hygroscopicity of the film formed is increased, and the stickiness is increased. As a monomer (b), there are acrylic acid, methacrylic acid and itaconic acid used alone or concomitantly.

Moreover, the monomer (c) provides the film formed with suitable hardness, softness, water solubility, etc., as required. As a monomer (c), there are, for example, methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, isopropyl (meth)acrylate, butyl (meth)acrylate, isobutyl (meth)acrylate, tertiary butyl (meth)acrylate, acrylonitrile, (meth)acrylamide, styrene, vinyltoluene, vinyl acetate, etc., used alone or concomitantly.

Furthermore, as another water-soluble polymer, it is possible to use a polymer prepared by carrying out solution polymerization of a monomer mixture of the following composition;

(d) diacetoneacrylamide : 5-88 wt%

(e) monomer represented by the general formula

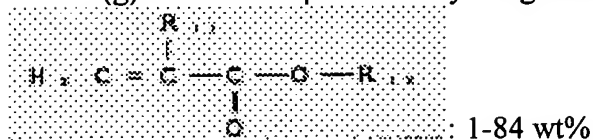


5-40 wt%

(where R_9 is H or CH_3 , and R_{10} is an alkyl group of C_8H_{17} - $\text{C}_{18}\text{H}_{37}$)

(f) at least one kind of monomer selected from a group comprising acrylic acid, methacrylic acid and itaconic acid: 6-35wt%

(g) monomer represented by the general formula



(where R₁₁ is H or CH₃, and R₁₂ is an alkyl group of CH₃-C₃H₇)

in a water-soluble solvent and adding a water-soluble organic base.

The monomer (d) itself is soluble in water, but it has a unique property that if its homopolymerization is carried out, the polymer formed becomes insoluble in water and hygroscopic. The amount of the monomer (d) compounded is less than 5 wt%, the hydrophilicity of the anionic polymer formed is insufficient, eliminating the affinity to hair, and the spreading of the solution on hair becomes poor. On the other hand, if the amount compounded is over 88 wt%, the film formed from the anionic polymer and resin mixture containing it becomes fragile, and it is undesirable considering the balance with the monomer (f) for improving hair-washability and monomer (g) for retaining film hardness and compatibility with a propellant.

If the amount of the monomer (e) compounded is less than 5 wt%, the film formed lacks softness, causing flaking. On the other hand, if the amount compounded is over 40 wt%, the anionic polymer formed becomes difficult to dissolve in water and at the same time, the hair-washing becomes difficult, and the stickiness of the film prepared is increased. As a specific example of the monomer (e), there are, for example, butyl (meth)acrylate, isobutyl (meth)acrylate, tertiary butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate, stearyl (meth)acrylate, etc., used alone or concomitantly.

If the amount of the monomer (f) compounded is less than 5 wt%, the film formed becomes difficult to dissolve in water. On the other hand, if it is over 35 wt%, the hygroscopicity of the film formed is high, and the stickiness is markedly increased. As a specific example of the monomer (f), there are, for example, acrylic acid, methacrylic acid and itaconic acid used alone or concomitantly.

Furthermore, the monomer (g) provides the film formed with suitable softness and bonding strength. As a specific example of the monomer (g), there are, for example, methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, isopropyl (meth)acrylate, etc., used alone or concomitantly.

The water-soluble anionic polymer of the former two monomers being useful as an aerosol or non-gas type setting agent is disclosed in Japanese Kokoku Patent Publication Nos. Sho 44[1969]-31238 and Sho 50[1975]-6538. The above polymer can be prepared, for example, by using an aliphatic alcohol having 1-4 carbon atoms as a solvent, peroxide such as benzoyl

peroxide, etc., or azo compound such as azobisisobutyronitrile, etc., as a polymerization initiator, carrying out the polymerization reaction at the boiling temperature of the solvent used or a temperature near it while stirring and, after polymerization, neutralizing with a water-soluble organic base so that the polymer formed becomes water soluble.

Furthermore, as another water-soluble anionic polymer, it is possible to use a polymer prepared by adding a water-soluble organic base to a butyl alcohol and (or) isopropyl alcohol ester of a copolymer of vinyl methyl ether and maleic anhydride. This polymer can be prepared by adding a water-soluble organic base to a commercially available polymer, for example "GANTREZES" (manufactured by US GAF Co.)

The cationic/amphoteric polymer and water-soluble anionic polymer cannot form good aerosol foam alone, but the resin composition of this invention prepared by combining them can form good aerosol foam without using any surfactant.

For example, the above resin composition is dissolved in water at a solid content in the range of 0.5-10 wt%, 80-95 wt% of the resin aqueous solution prepared and 20-5 wt% of a propellant are packed with pressure in an aluminum can with a resin coating to obtain an aerosol foam product. As a propellant, there are, for example, Freon, liquefied petroleum gas (LPG), solid carbon dioxide gas, etc., used alone or concomitantly. Incidentally, plasticizers such as higher alcohol esters of higher fatty acids, glycerol, polyethylene glycol, etc., luster-forming agents, coloring agents, hair nutrients, etc., are also suitably usable.

Furthermore, the above resin composition may be used as a component of hair lotion, hair cream, hair mist (non-gas aerosol), etc., by dissolving the above resin composition in water and (or) water-soluble solvent and adding hair-dressing additives.

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Incidentally, the (meth)acrylic acid used above means acrylic acid or methacrylic acid, the (meth)acrylate means acrylate or methacrylate, and the (meth)acrylamide means acrylamide or methacrylamide.

Application Examples 1-12

This invention is specifically explained by using application and comparative examples in comparison as follows. Incidentally, the "%" and "part" used are those by weight.

Table 1 shows the compositions (monomer compositions) of cationic/amphoteric polymers (partially including polymers with either cationization or amphoterization not carried out) used for Application Examples 1-12 and Comparative Examples 1-12 together with compositions of cationizing and amphoterizing agents used, mean molecular weight of polymer prepared and mole ratio of repeating units. In the table, the polymers shown with "CA 1-4" are

those within the restrictive range of Claim 1, and those shown with "CA 11-14" are those outside of the restrictive range of Claim 1.

Furthermore, Table 2 and Table 3 show the compositions (monomer compositions) of water-soluble anionic polymers used in Application Examples 1-10 and Comparative Examples 1-10 together with the compositions of the water-soluble bases used. In the tables, the polymers shown with "AN 1-4" are those within the restrictive range of Claim 2 or 3, and those shown with "AN 11-14" are those outside of the restrictive range of Claim 2 or 3. Incidentally, the procedures (polymerization, cationization, amphoterization and purification) used for those cationic/amphoteric polymers and those (polymerization and preparation) for the water-soluble anionic polymers used in the application and comparative examples are as follows.

Cationic/amphoteric polymer polymerization method

A four-necked flask equipped with a reflux condenser, thermometer, dropping funnel, glass tube of feeding nitrogen gas for substitution and stirrer was charged with 100 parts of monomers corresponding to respective repeating units, 50 parts of ethyl alcohol and 0.6 part of azobisisobutyronitrile, and the mixture was refluxed by heating at 80°C under a flow of nitrogen gas to carry out the polymerization reaction for 4 h.

Cationic/amphoteric polymer cationization method

Following the above polymerization reaction, an ethyl alcohol solution of a cationizing agent is added dropwise by using the dropping funnel. If the cationizing agent used is an acid, the reaction mixture is heated at 70-80°C under a flow of nitrogen gas for 1 h after the above addition in drops. If the cationizing agent used is a quaternary cationizing agent, a quaternary cationizing agent in its gaseous state is injected or its ethyl alcohol solution is added dropwise through the dropping funnel, and the mixture is heated at 70-80°C under a flow of nitrogen gas for 6 h to carry out the quaternary cationization reaction.

Cationic/amphoteric polymer amphoterization method

After the above cationization reaction, the amphoterization reaction is carried out. A suspension of sodium monochloroacetate or potassium monochloroacetate in a 30 wt% ethyl alcohol solution is added dropwise through the dropping funnel as an amphoterizing agent, and the mixture is heated at 70-80°C under a flow of nitrogen gas for 6 h to carry out the amphoterization reaction.

Cationic/amphoteric polymer purification method

The polymer solution obtained in the above amphoterization method has an inorganic salt precipitated forming a viscous suspension. It is purified by dissolving in ethyl alcohol, filtering

off the precipitates by using a pressurized filtering machine, and it is prepared as an ethyl alcohol solution with a solid content of 30%.

Polymerization and preparation of water-soluble anionic polymer

A four-necked flask similar to the one used for the above cationic/amphoteric polymer polymerization reaction is charged with 100 parts of the mixture of respective monomers, 50 parts of ethyl alcohol and 1.0 part of benzoyl peroxide, and the mixture is refluxed by heating at 80°C under a flow of nitrogen gas for 4 h to carry out the polymerization reaction. Subsequently, an ethyl alcohol solution of a water-soluble organic base is added dropwise through the dropping funnel, the mixture is stirred, and ethyl alcohol is added so that the solid content of the solution prepared is 40%.

Incidentally, the other water-soluble anionic polymer "GANTREZ-ES" was prepared by carrying out 30% neutralization of a commercially available polymer "GANTREZ-ES-425" (solid content of 50%) with amino methylpropanol as follows.

GANTREZ-ES-425 (solid content of 50%)	100 g
Amonomethylpropanol	11.7 g

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Table 1. Cationic/amphoteric polymer composition
(Unit used: gram on the top, No. of mole in the bottom inside ())

品番	重合に用いるモノマーの組成 (I) R ¹ (II) R ²	カチオン化剤		両性化剤		重合温度 (°C)	重合時間 (h)	重合率 (%)
		(I) R ¹ (II) R ²	(I) R ¹ (II) R ²	(I) R ¹ (II) R ²	(I) R ¹ (II) R ²			
GA-1	ジメチルアミノプロピルメタクリレート	171.9 (1.0)	エチルプロピレート	3.4 (0.05)	モノクロロ酢酸カリウム	122.5 (0.55)	12	3/33
GA-11	ジメチルアミノプロピルメタクリレート	171.9 (1.0)	—	—	モノクロロ酢酸カリウム	122.5 (0.55)	12	3/33
GA-12	ジメチルアミノプロピルメタクリレート	171.9 (1.0)	エチレンプロピレート	71.9 (0.5)	モノクロロ酢酸カリウム	122.5 (0.55)	12	10/33
GA-13	ジメチルアミノプロピルメタクリレート	171.9 (1.0)	エチレンプロピレート	71.9 (0.5)	—	—	14	100/33
GA-14	ジメチルアミノプロピルメタクリレート	171.9 (1.0)	酢酸	30.5 (0.5)	モノクロロ酢酸カリウム	122.5 (0.55)	12	38/33
GA-15	ジメチルアミノプロピルメタクリレート	171.9 (1.0)	酢酸	42.0 (0.7)	モノクロロ酢酸カリウム	122.5 (0.55)	12	16/33
GA-16	ジメチルアミノプロピルメタクリレート	171.9 (1.0)	3.5%塩酸	19.4 (0.3)	モノクロロ酢酸カリウム	122.5 (0.55)	14	10/34
GA-17	ジメチルアミノプロピルメタクリレート	171.9 (1.0)	3.5%塩酸	3.1 (0.05)	モノクロロ酢酸カリウム	122.5 (0.55)	14	3/33

- Key: 1 No.
2 Composition of monomers corresponding to respective repeating units
3 [I] and [II]
4 Cationizing agent
5 Amphoterizing agent
6 Mean molecular weight (10 thousand)
7 Mol% of repeating units [I]/[II]
8 Dimethylaminopropyl methacrylate

- 9 Dimethylaminoethyl methacrylamide
 10 Dimethylaminoethyl methacrylate
 11 Dimethylaminopropyl acrylamide
 12 Ethyl bromide
 13 Ethylene bromohydrin
 14 Acetic acid
 15 35% Hydrochloric acid
 16 Potassium monochloroacetate

Table 2. Composition of water-soluble anionic polymer
 (composition unit: part by weight)

試料	単量体の組成						可溶性基性物質	
	単量体(a)	単量体(b)	単量体(c)	—		—		
NR-1	2-エチルヘキシルアクリレート	14.9	アクリル酸	4.9	エチルアクリレート	12.9	アミノメチルプロパノール	12.9
			メタクリル酸	1.0	スチレン	6.0		
NR-11	2-エチルヘキシルアクリレート	45.0	アクリル酸	5.0	エチルアクリレート	33.0	アミノメチルプロパノール	12.0
			メタクリル酸	1.0	スチレン	6.0		
NR-2	ラウリルアクリレート	9.0	アクリル酸	16.0	n-ブチルアクリレート	19.0	モルホリン	53.0
	ラウリルメタクリレート	15.0	メタクリル酸	4.0	エチルメタクリレート	5.0		
NR-12	ラウリルアクリレート	5.0	アクリル酸	22.0	n-ブチルアクリレート	19.0	モルホリン	46.0
	ラウリルメタクリレート	13.0	メタクリル酸	3.0	エチルメタクリレート	9.0		

- Key: 1 No.
 2 Monomer composition
 3 Monomer (a)
 4 Monomer (b)
 5 Monomer (c)
 6 Organic base
 7 2-ethylhexyl acrylate
 8 Lauryl acrylate
 9 Acrylic acid
 10 Methacrylic acid
 11 Ethyl acrylate
 12 Styrene
 13 n-Butyl acrylate
 14 Aminomethylpropanol
 15 Morpholine

Table 3. Composition of water-soluble anionic polymer
(Composition unit: part by weight)

品名	単量体の組成							有機基特性物質		
	単量体 (a)	単量体 (b)	単量体 (c)	単量体 (d)	単量体 (e)	単量体 (f)				
1A-1	ジアセトンアクリルアミド	19.6	ステアリルメタクリレート	15.9	アクリル酸	4.3	メチルアクリレート	15.9	アミノメチルプロパンジオール	2.6
					メタクリル酸	2.3	メチルメタクリレート	10.3		
					イタコン酸	1.8				
1A-12	ジアセトンアクリルアミド	19.6	ステアリルメタクリレート	15.9	アクリル酸	1.9	メチルアクリレート	11.9	アミノメチルプロパンジオール	2.6
					メタクリル酸	2.3	メチルメタクリレート	10.3		
					イタコン酸	1.1				
1A-1	ジアセトンアクリルアミド	15.9	ステアリルメタクリレート	10.3	アクリル酸	8.4	エチルアクリレート	14.8	トリイソプロパノールアミン	27.8
					メタクリル酸	1.1	エチルメタクリレート	13.8		
					イタコン酸	2.8				
1A-14	ジアセトンアクリルアミド	15.9	ステアリルメタクリレート	10.3	アクリル酸	3.3	エチルアクリレート	1.8	トリイソプロパノールアミン	27.9
					メタクリル酸	7.5	エチルメタクリレート	1.8		
					イタコン酸	3.0				

- Key:
- 1 No.
 - 2 Monomer composition
 - 3 Monomer (d)
 - 4 Monomer (e)
 - 5 Monomer (f)
 - 6 Monomer (g)
 - 7 Organic base
 - 8 Diacetone acrylamide
 - 9 Lauryl methacrylate
 - 10 Stearyl methacrylate
 - 11 Acrylic acid
 - 12 Methacrylic acid
 - 13 Itaconic acid
 - 14 Methyl acrylate
 - 15 Methyl methacrylate
 - 16 Ethyl methacrylate
 - 17 Ethyl methacrylate
 - 18 Aminomethylpropanediol
 - 19 Tri-isopropanolamine

The cationic/amphoteric and water soluble anionic polymers prepared as described above were mixed in various mixing ratios to prepare various resin compositions of Application Examples 1-12 and Comparative Examples 1-12.

For the above resin compositions, aerosol foam was prepared with the following composition, and the performance was evaluated by carrying out the following test and evaluation methods. The results obtained are shown in Table 4.

Aerosol foam composition

Resin composition (solid content)	4 parts
Cetyltrimethylammonium chloride	0.2 part
Perfume	0.05 part
LPG	7 parts
Freon -12	1 part
Pure water	Remainder
Total	100 parts

Testing and evaluation methods

(1) Setting power (curl retention)

A hair sample about 22 cm long and about 2 g weight washed with a commercially available shampoo product, rinsed with a commercially available conditioner and dried in air was coated with a aerosol foam of about a quail-egg size, the foam was spread with fingers, and the treated hair sample was curled on a curler of 1.2 cm diameter. It was dried at 55-60°C for 30 min and cooled in a desiccator. Subsequently, it was released from the curler in a spiral shape, attached to a vertically standing glass plate (with 0.5 cm interval scale marks) and placed in a constant temperature and constant humidity dryer set at 30°C and 90%RH. After 10 h, the position of the tip of the test sample was recorded, and the curl-retention rate was determined by using the following formula.

$$\text{Curl-retention rate (\%)} = (L - L_t) / (L - L_o) \times 100$$

L: length when the sample is stretched (L = 22 cm)

L_o : position of the tip of the sample before placing in a constant temperature and constant-humidity dryer

L_t : position of the tip of the sample before placing in a constant temperature and constant humidity dryer for 10 h

(2) Flaking

A hair sample prepared similar to the setting-power evaluation was combed, and the amount of resin dropped out was evaluated as follows.

O: hardly any resin dropping, Δ : slight resin dropping, X: marked resin dropping

(3) Smoothness

The ease of combing at the time of flaking evaluation was evaluated as follows.

O: easy combing, Δ : slightly difficult combing, X: difficult combing

(4) Film properties (washability and blocking)

A constant amount of a solution of aerosol foam before adding a propellant was taken on a glass plate and spread to an approximately constant area by using a glass rod. The glass plate was allowed to stand in an atmosphere of 20°C and 60%RH for a day and dried subsequently at 60°C for 1 h.

For the washability, the glass plate was soaked in an aqueous solution containing 0.5% of a commercially available shampoo product, and the state of film dissolution was evaluated as follows.

O: dissolution within 1 h, Δ: small amount remained after 1 h, X: large amount remained after 1 h

For the blocking (stickiness), the glass plate was placed in a constant temperature and constant humidity dryer set at 30°C and 90%RH for one day, and the finger-touch examination was used to evaluate as follows.

O: no stickiness, Δ: slight stickiness, X: marked stickiness

(5) Foam quality

An aerosol foam sample of a quail-egg size was sprayed onto a glass plate, the foam was pressed with a finger, and the elasticity of the foam was evaluated as follows.

O: elastic, Δ: slightly lacking elasticity, X: no elasticity

(6) Foaming ability

An aerosol foam sample of a quail-egg size was sprayed onto a paper filter, and the continuation of the foaming state was evaluated as follows.

O: hardly any change for 30 sec or longer, Δ: shrinking tendency in 10-30 sec, X: foam disappearance as soon as it is sprayed

(7) Feel

A hair sample prepared similarly to that for flaking evaluation was touched by a hand to evaluate the feel as follows.

O: soft and good feel, D: slight roughness or stickiness, X: marked roughness or stickiness

Table 4. Aerosol foam performance evaluation

種 類	樹脂組成物の組成 (重量比)				セ ッ チ ン グ	フ レ ー ミ ン グ	保 持 性	洗 浄 性	ア ロ マ ー	質	泡 量	泡 密
	カチオン/両 性ポリマー		水溶性アニオ ンポリマー									
実施例 1	CA-1	1	AA-1	19	80	○	○	○	○	○	○	○
比較例 1	CA-1	1	AA-1	17	83	△	△	○	○	△	△	○
実施例 2	CA-2	1	AA-2	2	80	○	○	○	○	○	○	○
比較例 2	CA-2	1	AA-2	1	88	○	△	○	△	○	○	△
実施例 3	CA-3	1	AA-3	1	88	○	○	○	○	○	○	○
比較例 3	CA-3	1	AA-3	5	85	○	○	○	△	×	×	△
実施例 4	CA-3	1	AA-4	5	88	○	○	○	○	○	○	○
比較例 4	CA-12	1	AA-4	5	74	○	○	×	○	○	○	△
実施例 5	CA-2	1	AA-2	5	85	○	○	○	○	○	○	○
比較例 5	CA-13	1	AA-2	5	85	○	○	×	○	○	○	△
実施例 6	CA-4	1	AA-4	3	88	○	○	○	○	○	○	○
比較例 6	CA-14	1	AA-4	5	72	○	○	○	△	△	△	○
実施例 7	CA-3	1	AA-1	7	87	○	○	○	○	○	○	○
比較例 7	CA-3	1	AA-11	7	58	○	×	○	×	○	○	×
実施例 8	CA-4	1	AA-2	1	88	○	○	○	○	○	○	○
比較例 8	CA-4	1	AA-12	1	89	○	○	○	×	○	○	△
実施例 9	CA-2	1	AA-3	7	93	○	○	○	○	○	○	○
比較例 9	CA-1	1	AA-13	1	80	○	○	×	○	△	△	×
実施例 10	CA-1	1	AA-4	7	90	○	○	○	○	○	○	○
比較例 10	CA-1	1	AA-14	7	84	○	△	△	×	○	○	△
実施例 11	CA-3	1	CANTREX	10	80	○	○	○	○	○	○	○
比較例 11	CA-3	1	CANTREX	17	82	△	△	○	○	△	△	△
実施例 12	CA-4	1	CANTREX	2	79	○	○	○	○	○	○	○
比較例 12	CA-4	1	CANTREX	1	81	○	△	○	△	○	○	△

- Key: 1 Kind
 2 Resin composition (solid content weight ratio)
 3 Cationic/amphoteric polymer
 4 Water-soluble anionic polymer
 5 Setting power
 6 Flaking
 7 Smoothness
 8 Washability
 9 Blocking
 10 Foam quality
 11 Foaming ability
 12 Handle
 13 Application Example ____
 14 Comparative Example ____

Effect of the invention

As described above in detail, the hair-dressing resin composition and aerosol foam soap-free composition of this invention show hair-dressing effects showing no stickiness or

flaking, having excellent smoothness and exhibiting excellent setting power without any damage in the feel at a high temperature under high humidity.